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**Thermodynamic Modeling of Calcium Sulfate Hydrates in the CaSO4-H2O System from 273.15 to 473.15 K with Extension to 548.15 K**

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ABSTRACT: Calcium sulfate is one of the most common inorganic salts with a high scaling potential. The solubility of calcium sulfate was modeled with the Pitzer equation at a temperature range from 273.15 to 473.15 K from published solubility data, which was critically evaluated. Only two Pitzer parameters, $\beta^{(1)}$ and $\beta^{(2)}$, with simple temperature dependency are required to model the solubility with excellent extrapolating capabilities up to 548.15 K. The stable temperature range for gypsum is 273.15–315.95 K, whereas above 315.95 K the stable phase is anhydrite. Hemihydrate is in the metastable phase in the whole temperature range, and the obtained metastable invariant temperature from gypsum to hemihydrate is 374.55 K. The obtained enthalpy and entropy changes at 298.15 K for the solubility reactions are in good agreement with literature values yielding solubility products of $2.40 \times 10^{-5}$, $3.22 \times 10^{-8}$, and $8.75 \times 10^{-8}$ for gypsum, anhydrite, and hemihydrate, respectively. The obtained Pitzer model for the $\text{CaSO}_4$–$\text{H}_2\text{O}$ system is capable of predicting the independent activity and osmotic coefficient data with experimental accuracy. The mean absolute average error of activity coefficient data at 298.15 K is less than 2.2%. Our model predicts the osmotic coefficient on the ice curve within 1.5% maximum error.

1. INTRODUCTION
Scaling or precipitation fouling, mainly forming a solid layer on equipment surfaces or piping networks, is a persistent problem encountered in many industrial processes, causing production losses, standstills, downtime and process efficiency decrease due to the reduction of equipment volume and material flow, increased heat transfer resistance, corrosion, and wearing out of construction materials. Hence, scaling prevention and techniques for evaluating scaling tendencies are of considerable practical and theoretical importance in science and the engineering field.

Calcium sulfate is one of the most common inorganic salts with a high scaling potential in oil and gas production, water desalination, geothermal energy production, sulfur dioxide removal from flue gas by coal-fired power plants, and hydrometallurgical processes of zinc, nickel, copper, and tungsten. The demand for utilization of membrane technology is increasing and thus creating requirement for a better understanding of the solubility behavior of calcium sulfate. Moreover, the demand for process water circulation in hydrometallurgical processes will build up more and more complex and concentrated aqueous solutions, increasing the possibility of scaling. Thus, the need of thermodynamic understanding of a multicomponent aqueous solution is required, since laboratory analyses only, are not enough to comprehend the scaling potential and its variations with temperature and concentration.

In aqueous solutions, calcium sulfate forms stable hydrates with 0, 1/2, and 2 molecules of crystalline water, with the chemical names of anhydrite (AH: $\text{CaSO}_4$), hemihydrate (HH: $\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$), and dihydrate, i.e., gypsum (DH: $\text{CaSO}_4\cdot2\text{H}_2\text{O}$). The stability regions of $\text{CaSO}_4$ hydrates depend on solution conditions, and they are influenced by temperature and composition of the aqueous solution. Therefore, understanding the phase equilibria of $\text{CaSO}_4$ as a function of temperature and other electrolytes is of great theoretical significance and practical importance, making it possible to estimate its scaling potential and facilitate the synthesis of calcium sulfate materials in industrial processes.

Applying the CALPHAD methodology, the thermodynamic description of the binary $\text{CaSO}_4$–$\text{H}_2\text{O}$ system is fundamental to clarify the thermodynamic behavior of calcium sulfate and its hydrates in aqueous solutions.
The aim of this study was to compile and reassess critically the experimental data of calcium sulfate and model the thermodynamic behavior of the CaSO$_4$–H$_2$O system up to 473.15 K. The assessment procedure was similar as used earlier for FeSO$_4$–H$_2$O, MnSO$_4$–H$_2$O, and NiSO$_4$–H$_2$O systems. All experimental data used in the modeling were taken from the literature and reviewed critically. The resulting thermodynamic model was obtained using the thermodynamic equilibrium calculation program MTDATA, which uses Gibbs energy minimization routine and includes the Pitzer activity coefficient model for aqueous solutions. The CALPHAD method was used in modeling to ensure internal consistency of the thermodynamic data. Furthermore, the modeling results were compared with the experimental data and other similar models to validate the accuracy of the present model and critical analysis in detail.

### 2. THERMODYNAMIC DATA

A large number of solubility measurements have been carried out for gypsum, hemihydrate, and anhydrite since the middle of 19th century. Most of the solubility data are in agreement with each other, in spite of slight deviations. However, a large controversy exists on transition temperatures between various calcium sulfate hydrates in the CaSO$_4$–H$_2$O system. The main reason for this problem is kinetic hindrance during phase change. Anhydrite does not crystallize with a measurable rate from water below 343.15 K, even in the presence of anhydrite seeds, and does not hydrate in several months to gypsum without gypsum seeds present.

Freyer and Voigt reviewed the solubility of gypsum, hemihydrate, and anhydrite in the temperature range (273.15–473.15) K at saturation pressure and pointed out that at low temperatures the stable phase is gypsum, at high temperatures it is anhydrite, whereas hemihydrate remains metastable at all temperatures. The borderslines of the solubility data points yield a transition temperature between gypsum–anhydrite from about 298.15 to 325.15 K. Within the scatter of the solubility data, the possible transition temperature of gypsum–hemihydrate phase change covers a range from less than 353.15 K to nearly 383.15 K.

On the basis of the review of Freyer and Voigt, Present drew the solubility curves for gypsum, hemihydrate, and anhydrite at saturation pressure up to 523.15 K and concluded that in pure water, the gypsum–anhydrite phase transition occurs between 298.15 and 325.15 K on the basis of solubility measurements of the phases, and the gypsum–hemihydrate transition occurs between 352.15 and 382.15 K.

Recently, Krumgalz summarized the solubility of calcium sulfate in the temperature range between 273.15 and 681.15 K covered by 110 publications starting from 1843. He determined that the transition temperatures of gypsum–anhydrite, gypsum–hemihydrate, and hemihydrate–anhydrite
are 318.76, 373.85, and 471.55 K, respectively, according to the polynomial equation curves. He used a six-order polynomial for the solubility of anhydrite and four-order polynomials for hemihydrate and gypsum. He also gave several reasons for the relatively large scatter of the solubility data of calcium sulfate determined by different authors.

In this work, all experimental data were taken from the available literature. The data with less than three experimental data points in one paper or series were not considered in the modeling to obtain reasonable and reliable fitting results depending on temperature. Especially, the experimental data for anhydrite and hemihydrate under metastable conditions were critically analyzed, such as the data from 273.15 to 383.15 K for noncrystalline hemihydrate by D’Ans et al.16 as well as data for more soluble polyformic forms such as \(\beta\)-anhydrite in the temperature range (278.15–383.15) K by Sborgi and Bianchi17 and also \(\beta\)-anhydrite and \(\beta\)-hemihydrate in the temperature range (308.15–383.15) K by Power and Fabuss.18 All of these metastable data were excluded. The solubility of gypsum measured by Farrah et al.19 is regularly lower than other data, so it was also excluded completely from the assessment but retained for the result comparison.

All solubility data were converted to molality, mol/kg-H\(_2\)O. The values of 136.14 and 18.015 g/mol were adopted for the molar mass of CaSO\(_4\) and H\(_2\)O, respectively, in the data conversion to obtain accurate data. The considered solubility data of calcium sulfate in water is collected in Table 1. The temperature ranges of gypsum, anhydrite, and hemihydrate in the table are (273.15–388.15), (273.15–681.15), and (273.15–473.15) K, respectively. All data above 473.15 K were reserved for testing the extrapolation capabilities. The criteria used to exclude or include a data point in the assessment are discussed in Section 4.1 in detail.

### 3. Computational Methods

#### 3.1. Pitzer Interaction Model

The Pitzer model, one of the most widely used activity coefficient models, has been extensively used for modeling thermodynamic properties of aqueous electrolyte systems. Pitzer and his cooperators gave details of the model in the literature.\(^{41–43}\) It was developed by combining the expression of Debye–Hückel electrostatic theory for long-range interactions and composition for short-range ion-specific interactions with a virial-type expansion. Harvie and Weare\(^{44}\) and Harvie et al.\(^{45}\) further included unsymmetrical electrostatic mixing terms in the modified Pitzer model to improve the fit in multicomponent systems.

The mathematical expression and internal parameters of the model are clarified in eqs 1–6. Equation 1 reproduces the Debye–Hückel type contribution of the dilute solution domain. Equation 2 describes the stochiometric mean activity coefficient \(\ln \gamma_x\), eq 3 formulates the osmotic coefficient \(\phi\), eqs 4 and 5 give the concentration dependence of the electrolyte specific terms \(B^\phi\) and \(B\), and eq 6 further explains the function \(g(x)\) for eq 5.

\[
f^\phi = -A_\phi \left[ \frac{\sqrt{T}}{1 + b \sqrt{T}} + \left( \frac{2}{b} \right) \ln(1 + b \sqrt{T}) \right]
\]  

\[
\ln \gamma_x = z_M^x \ln \phi + 2m \left( \frac{\nu_{MX}}{\nu} \right)^2 (B^\phi_{MX} + B_{MX})
\]

\[
\phi - 1 = -A_\phi \gamma_x z_M^x \left[ \frac{1^{1/2}}{(1 + b \sqrt{T})} \right] + 2m \left( \frac{\nu_{MX}}{\nu} \right)^2 B^\phi_{MX}
\]

\[
B^\phi_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_{I}^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_{I}^{1/2})
\]

\[
B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \alpha_{I}^{0.5} + \beta_{MX}^{(2)} \alpha_{I}^{0.5}
\]

\[
g(x) = 2 \left[ 1 - (1 + x)e^{-x} \right]^{-1}
\]

where \(A_\phi\) is the Debye–Hückel parameter, \(\nu\) is the sum of the stoichiometric coefficients of cation (\(\nu_M\)) and anion (\(\nu_x\)), \(z\) is charge, \(b\) is an electrolyte-independent constant \((b = 1.2)\), and the parameter values \(\alpha_I\) and \(\alpha_z\) used for 2–2 electrolyte of the Pitzer model are 1.4 and 12, respectively, in this work.

Thus, the electrolyte specific parameters to be assessed are \(\beta_{MX}^{(0)}\) \(\beta_{MX}^{(1)}\) \(\beta_{MX}^{(2)}\) \(\gamma_{MX}^{(0)}\) \(\gamma_{MX}^{(1)}\) \(\gamma_{MX}^{(2)}\) \(g(x)\) for eq 4 but with different values for the internal constants. The constant values used in the above equations are the same as suggested by Pitzer\(^{41}\) and also adopted by Harvie et al.\(^{44,45}\) even though different values have been used in many approaches of the Pitzer formalism.\(^{46–48}\)

### 3.2. Thermodynamic Functions

The solubility products \(K\) of the solid phases for calcium sulfate hydrates are expressed by the following eqs 7–12:

\[
\text{CaSO}_4\cdot2\text{H}_2\text{O}(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O}(l)
\]

\[
\text{CaSO}_4\cdot0.5\text{H}_2\text{O}(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 0.5\text{H}_2\text{O}(l)
\]

\[
\text{CaSO}_4(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)
\]

\[
K_{\text{DH}} = \frac{a_{\text{Ca}^{2+}(aq)} a_{\text{SO}_4^{2-}(aq)} a_{\text{H}_2\text{O}(l)}}{a_{\text{CaSO}_4\cdot2\text{H}_2\text{O}(s)}} = \gamma_{\text{Ca}^{2+}}^2 \gamma_{\text{SO}_4^{2-}}^2
\]

\[
K_{\text{AH}} = \frac{a_{\text{Ca}^{2+}(aq)} a_{\text{SO}_4^{2-}(aq)}^{0.5} a_{\text{H}_2\text{O}(l)}}{a_{\text{CaSO}_4\cdot0.5\text{H}_2\text{O}(s)}} = \gamma_{\text{Ca}^{2+}}^2 \gamma_{\text{SO}_4^{2-}}^{0.5}
\]

where concentration unit \(m\) is the molality of CaSO\(_4\) (mol/kg of water), used throughout this paper. Activities of pure solid phases are assumed to be 1, that is, their thermodynamic properties are insensitive to pressure.
Table 2. Tested Models for the Optimization of Pitzer Parameters in the Assessment

<table>
<thead>
<tr>
<th>model</th>
<th>OF value</th>
<th>number of fitted terms in parameters</th>
<th>parameters for Ca(^{2+})–SO(_4^{2-}) ion interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.70</td>
<td>4</td>
<td>(\beta(0)) A</td>
</tr>
<tr>
<td>D</td>
<td>0.12</td>
<td>4</td>
<td>(\beta(1)) x</td>
</tr>
<tr>
<td>E</td>
<td>0.10</td>
<td>4</td>
<td>(\beta(1)) x</td>
</tr>
<tr>
<td>F</td>
<td>0.07</td>
<td>6</td>
<td>(\beta(1)) x</td>
</tr>
<tr>
<td>G</td>
<td>0.08</td>
<td>5</td>
<td>(\beta(1)) x</td>
</tr>
<tr>
<td>H</td>
<td>0.08</td>
<td>5</td>
<td>(\beta(1)) x</td>
</tr>
<tr>
<td>I</td>
<td>0.13</td>
<td>5</td>
<td>(\beta(1)) 0.15</td>
</tr>
<tr>
<td>J</td>
<td>0.10</td>
<td>4</td>
<td>(\beta(1)) 0.15</td>
</tr>
<tr>
<td>K</td>
<td>0.12</td>
<td>4</td>
<td>(\beta(1)) x</td>
</tr>
</tbody>
</table>

The temperature dependency of Gibbs energy change of forming the solid phase according to eqs 7–9 is expressed in the following form (eq 13)

\[
\Delta G^o(T) = -RT \ln K_{SP} = A_C + B_C \left(\frac{T}{K}\right) + C_C \left(\frac{T}{K}\right) \ln \left(\frac{T}{K}\right) + D_C \left(\frac{T}{K}\right)^2 + E_C \left(\frac{T}{K}\right)^3 + F_C \left(\frac{T}{K}\right)^{-1}
\]

The general temperature dependency of the parameters in MTDATA for the Pitzer equation (p) is

\[
p = A_{Piz} + B_{Piz} \left(\frac{T}{K}\right) + C_{Piz} \left(\frac{T}{K}\right) \ln \left(\frac{T}{K}\right) + D_{Piz} \left(\frac{T}{K}\right)^2 + E_{Piz} \left(\frac{T}{K}\right)^3 + F_{Piz} \left(\frac{T}{K}\right)^{-1}
\]

3.3. Parameter Optimization. MTDATA version 6.0 was used for parameter fitting in this work. In MTDATA, there are several excess Gibbs energy models available, including the Pitzer equation with Harvie et al.\(^\text{35}\) modification and the NPL Pitzer model.\(^\text{49}\) It solves thermodynamic equilibrium by using the Gibbs energy minimization technique and includes several pure substance databases and a number of excess Gibbs energy models for different kinds of solutions. It also has an assessment module to fit model parameters from experimental data. The objective function (OF) used in MTDATA is

\[
OF = \sum_{i=1}^{N} \frac{(C_i - E_i)^2}{U_i}
\]

where \(w_i\) is the weight of the experimental value, \(C_i\) is the calculated value, \(E_i\) is the experimental value, and \(U_i\) is the uncertainty. All weights for the adopted experimental data, except for rejected values, were set to 1 in the assessment.

The goodness of the assessment for each experimental data point was estimated by the absolute percentage error, defined as

\[
APE = \frac{|C_i - E_i|}{E_i} \times 100\%
\]

4. RESULTS AND DISCUSSION

4.1. Fitting Parameters. Due to the small values for solubilities of calcium sulfate hydrates in water, a new optimization approach was tested. Instead of comparing the calculated and measured molality, the difference in Gibbs energy was selected to fit the parameters of the Pitzer model. According to eq 13, at solubility limit, \(\Delta G^o(T) + RT \ln K_{SP} = 0\). Thus, we obtain

\[
C_i = \Delta G^o(T)
\]

\[
E_i = RT \ln K_{SP}
\]

The uncertainty \(U_i\) was set to 100 J/mol for stable phases, whereas 500 J/mol was used for metastable phases. Only first three parameters \(A_C - C_G\) were found be adequate to describe \(\Delta G^o(T)\).
The optimized Pitzer parameters of model D obtained in this work are given in Table 4, containing the parameters collected from previous works. The total number of fitted terms in Pitzer parameters is only four in our model compared with six terms in the model of Wang et al. and nine terms in the model of Raju and Atkinson. Wang et al. modeled the solubility of CaSO4 in sulfuric acid CaSO4·H2SO4·H2O system in the temperature range from 298.15 to 368.15 K, whereas Raju and Atkinson modeled the solubility in CaSO4·NaCl·H2O system between 273.15 and 573.15 K. Both Wang et al. and Raju and Atkinson used literature values of Pitzer parameters from 298.15 K in their models: Pitzer and Mayorga and Rogers, respectively. Raju and Atkinson also extracted the temperature dependency for CaSO4 Pitzer parameters from published values for MgSO4.

The HMW50, SMW51 models also used only four terms in their Pitzer parameters, but they included a neutral ion pair CaSO4(aq) in their model with two to three terms depending on temperature.

The relative errors, (Ci − Ei)/Ui, between calculated (Ci) and “experimental” (Ei) values for precipitation reactions of calcium sulfate were plotted in Figure 1, in which the solid symbol means the included value whereas the hollow one means the excluded value in the assessment.

The uncertainty used for stable-phase equilibrium was 100, and 500 J/mol was used for the unstable one. Most values of the errors were close to zero. The data for gypsum and hemihydrate are in good agreement, whereas the experimental data for anhydrite deviate to some degree at high temperature. Only three anhydrite data points above temperature 373.15 K were accepted in the assessment. Thus, the assessment at about 373.15 K is based mostly on solubility of hemihydrate.

The assessed temperature dependencies of Gibbs energy for calcium sulfate hydrates in the assessment. Only three anhydrite data points above temperature 373.15 K were accepted in the assessment. Thus, the assessment at about 373.15 K is based mostly on solubility of hemihydrate.

The temperature ranges used in the assessment were 273.15–388.15, 273.15–423.15, and 273.15–473.15 K for gypsum, anhydrite, and hemihydrate, respectively (Table 5).
optimized parameters of this work. The solubility curves of each phase depending on temperature are drawn together with all collected experimental data. Predictions by recent models are also shown. The obtained difference between calculated and experimental molality for calcium sulfate hydrates is also shown in figures, where the solid symbol means the adopted value and the hollow one refers to data rejected in the assessment. The goodness of the assessment for adopted experimental data is estimated by standard deviation (SD), also known as root mean square error, defined as

$$\text{SD} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (C_i - E_i)^2}$$

where \(i\) goes over all experimental points (\(N\)) with nonzero weights in the experimental set and \(C_i\) is the calculated and \(E_i\) is the experimental molality. The mean absolute percentage error (MAPE), also known as the absolute average relative deviation (AARD %), is used when the focus is on relative deviation

$$\text{MAPE} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{C_i - E_i}{E_i} \right|$$

The standard deviation values for fitted data are 0.00045 mol/kg for gypsum, 0.00063 mol/kg for anhydrite, and 0.0053 mol/kg for hemihydrate. The mean absolute percentage errors (MAPE), are 2.2, 2.5, and 7.3%, respectively.

**4.2.1. Gypsum.** As shown in Figure 2a,b, the calculated solubility values for gypsum are consistent with the most experimental solubility data. The temperature dependency of the solubility curve goes through most data points. Most of the differences between calculated and experimental data for gypsum are less than 0.001 mol/kg-H_2O, with the absolute percentage error within 5%.

However, excluded points show a slight scatter, such as the data points at 273.15 K by D’Ans et al., 16 273.65 K by Marshall and Slusher,26 as well as data points at 298.15 K by Block and Waters16 and at 303.15 K by Bock.29 Still, the modeled curve around 273.15 K goes between these two rejected data points. In addition, the excluded data from Farrah et al.19 are scattered and lower than others. The absolute percentage errors between the calculated and experimental data for these excluded observations are above 5%.

**4.2.2. Anhydrite.** The calculated phase boundary for anhydrite performs excellently with the optimized parameters in the temperature range of 273.15–573.15 K, as presented in Figure 3a,b, even though the assessment of Gibbs energy according to solubility data shows high scatter at temperatures above 373.15 K in Figure 1.

**4.2.3. Hemihydrate.** Compared with gypsum and anhydrite, hemihydrate is considered as the metastable phase and attracts
less attention from other researchers. The assessed solubility and differences with predicted and measured solubilities are presented in Figure 4a,b from 273.15 to 473.15 K. The calculated phase boundaries agree with the experimental data very well. All data, except the data points at 463.15 and 473.15 K by D’Ans et al.,16 were included in the assessment. The difference between the calculated and experimental saturation boundaries is a little larger at low temperatures, whereas the absolute percentage errors were less than 10%, due to the large values of solubility. Most of the absolute percentage errors were still within 5%, showing a good modeling capability of the present parameter set.

4.3. Transition Temperature. The transformations of calcium sulfate hydrates are of significant importance for CaSO₄−H₂O system to predict and control calcium sulfate formation. However, a large controversy exists between the phase equilibria regarding the various calcium sulfate hydrates in the CaSO₄−H₂O system. The transition temperatures for calcium sulfate dehydration are summarized and listed in Table 6.

From the solubility curves calculated in this work (Figure 5), the estimated transition temperature of gypsum to anhydrite is 315.95 K. This agrees with the research result of 315.15 ± 2 K from Azimi.1 D’Ans,16,57 Hill,36 Posnjak,58 Kelly et al.,59 Macdonald,60 Zen,65 Cruft and Chao,66 Grigor’ev and Shamaev,67 Corti and Fernandez-Prini,68 and Kontrec et al.,69 and is in the temperature intervals determined by Freyer and Voigt11 and Present.14 The transition temperature of gypsum to hemihydrate has drawn less attention and it is in this study determined at 374.55 K, in agreement with Krumgalz’s15 value of 373.95 K but a little bit higher as obtained by Posnjak’s. Still, the stable temperature range is 273.15–315.95 K for gypsum and above 315.95 K for anhydrite whereas hemihydrate is in a metastable phase in the whole temperature range. The transition temperature of anhydrite to hemihydrate suggested recently by Krumgalz15 is considered incorrect since after 471.55 K, hemihydrate would be in a stable phase instead.
of anhydrite, which is most unlikely and has never been reported to our knowledge.

4.4. Comparison with Previous Works. The CaSO$_4$−H$_2$O system has been assessed with the Pitzer model by many authors, but most of them calculated the solubilities of gypsum and anhydrite only and did not include hemihydrate. Møller$^{50}$ described a chemical equilibrium model for CaSO$_4$−H$_2$O system on the basis of Pitzer equations, with gypsum from 298.15 to 383.15 K and anhydrite and hemihydrate from 298.15−498.15 K. But the parameter $\beta(0) = 0.15$ is different from the later obviously mistyped value of 0.015 reported by Greenberg and Møller.$^{52}$ Moreover, they have used the ion pair CaSO$_4$(aq) in their model with two separate temperature ranges and parameter sets. So their model was not used to compare the observation in this work.

The assessed model of Wang et al.$^{21}$ and the one by Raju and Atkinson$^{53}$ were used to compare the parameterization of this work. Wang et al.$^{21}$ modeled CaSO$_4$−H$_2$O system in the temperature range 298.15−363.15 K as a subsystem of the CaSO$_4$−H$_2$SO$_4$−H$_2$O system, and Raju and Atkinson,$^{53}$ in the temperature range 273.15−573.15 K as a subsystem of the CaSO$_4$−NaCl−H$_2$O system.

The temperature dependencies of Pitzer parameters and forming Gibbs energy changes of solid phases are listed in Tables 4 and 5.

The simulation results were drawn in Figures 2−4, together with the experimental data collected in this work. Wang et al.$^{21}$ simulated gypsum and anhydrite primary phase fields with a temperature range of 298.15−363.15 K. We extended the temperature ranges from 273.15 to 393.15 and 273.15 to 573.15 K for gypsum and anhydrite, respectively. The model of Wang et al. shows excellent trends and is close to our results. But the extrapolated solubilities for anhydrite calculated by parameters of Wang et al. at low temperatures of 273.15−298.15 K are larger than the experimental data whilst our model predicts lower values.

Raju and Atkinson$^{53}$ present an insufficient model for gypsum at 273.15−393.15 K and anhydrite at 273.15−573.15 K. The solubilites of gypsum from Raju and Atkinson are smaller than the experimental data, the data calculated by

Table 6. Transition Temperatures for Calcium Sulfate Dehydration

<table>
<thead>
<tr>
<th>reaction</th>
<th>transition temperature (K)</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO$_4$·2H$_2$O $\rightleftharpoons$ CaSO$_4$ + 2H$_2$O</td>
<td>315.95</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>317.85$^a$</td>
<td>Wang et al., 2013$^{21}$</td>
</tr>
<tr>
<td></td>
<td>333.05</td>
<td>Raju and Atkinson, 1990$^{53}$</td>
</tr>
<tr>
<td></td>
<td>313.15 ± 2</td>
<td>Azimi, 2010$^1$</td>
</tr>
<tr>
<td></td>
<td>318.76</td>
<td>Krumgalz, 2018$^{15}$</td>
</tr>
<tr>
<td></td>
<td>≈313.15</td>
<td>D’Ans, 1933, D’Ans et al., 1955$^{56}$</td>
</tr>
<tr>
<td></td>
<td>315.15 ± 2</td>
<td>Hill, 1937$^{36}$</td>
</tr>
<tr>
<td></td>
<td>315.15 ± 2</td>
<td>Posnjak, 1938$^{58}$</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>Kelly et al., 1941$^{10}$</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>Macdonald, 1953$^{50}$</td>
</tr>
<tr>
<td></td>
<td>322.65 ± 2.5</td>
<td>Knacke and Gans, 1977$^{71}$</td>
</tr>
<tr>
<td></td>
<td>322.65 ± 2.5</td>
<td>Møller, 1988$^{52}$</td>
</tr>
<tr>
<td></td>
<td>328.65 ± 1.5</td>
<td>Hardie, 1967$^{72}$</td>
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<tr>
<td></td>
<td>331.15 ± 2</td>
<td>Blount and Dickson 1973$^{63}$</td>
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<tr>
<td></td>
<td>329.15 ± 3</td>
<td>Van’t Hoff et al., 1903$^{54}$</td>
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<td></td>
<td>333.05</td>
<td>Raju and Atkinson 1990$^{53}$</td>
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<td></td>
<td>336.65</td>
<td>Zen, 1965$^{55}$</td>
</tr>
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<td>319.15 ± 2.5</td>
<td>Zen, 1965$^{55}$</td>
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<tr>
<td></td>
<td>≈313.15</td>
<td>Cruft and Chao, 1970$^{60}$</td>
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<tr>
<td></td>
<td>≈313.15</td>
<td>Grigor’ev and Shamaev, 1976$^{67}$</td>
</tr>
<tr>
<td></td>
<td>315.75 ± 0.4</td>
<td>Corti and Fernandez-Prini, 1983$^{66}$</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>Kontrec et al., 2002$^{29}$</td>
</tr>
<tr>
<td></td>
<td>374.55</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>373.95</td>
<td>Krumgalz, 2018$^{15}$</td>
</tr>
<tr>
<td></td>
<td>370.15 ± 1</td>
<td>Posnjak, 1938$^{58}$</td>
</tr>
<tr>
<td></td>
<td>363.65</td>
<td>Ostroff, 1964$^{70}$</td>
</tr>
<tr>
<td></td>
<td>471.55$^b$</td>
<td>Krumgalz, 2018$^{15}$</td>
</tr>
</tbody>
</table>

| CaSO$_4$·2H$_2$O $\rightleftharpoons$ CaSO$_4$·0.5H$_2$O + 1.5H$_2$O |
|---------------------------|--------|
| CaSO$_4$·0.5H$_2$O $\rightleftharpoons$ CaSO$_4$ + 0.5H$_2$O |

$^a$Value calculated by MTDATA with Wang et al. parameters, value of about 315 K reported by Wang et al. 2013. $^b$Considered as incorrect, hemihydrate is in metastable phase at all temperature ranges.
Table 7. Thermodynamics for Calcium Sulfate Solubility Reaction at 298.15 K

<table>
<thead>
<tr>
<th>H2O(s)</th>
<th>CaSO4·2H2O(s) = Ca2+(aq) + SO4²⁻(aq) + 2H2O(l)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/(K mol))</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raju and Atkinson, 1990 53</td>
<td>26.241</td>
<td>−577°</td>
<td>−89.95°</td>
<td>2.53 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>Wang et al., 2013 21</td>
<td>26.284</td>
<td>5217°</td>
<td>−70.66°</td>
<td>2.48 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>26.372</td>
<td>−1814</td>
<td>−94.54</td>
<td>2.40 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>HSC 954</td>
<td>25.671</td>
<td>−1716</td>
<td>−91.86</td>
<td>3.18 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>NBS 71</td>
<td>24.893</td>
<td>−1130</td>
<td>−87.28</td>
<td>4.36 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>CODATA 72</td>
<td>26.140</td>
<td>−1130</td>
<td>−91.46</td>
<td>2.63 × 10⁻⁵</td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Comparison of the Pitzer Models between This Work and Previous Studies

<table>
<thead>
<tr>
<th>reference</th>
<th>number of terms in Pitzer parameters</th>
<th>parameter temperature range (K)</th>
<th>ΔH° 298 (kJ/mol)</th>
<th>ΔS° 298 (J/(K mol))</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>4</td>
<td>273.15–473.15</td>
<td>315.95</td>
<td>374.55</td>
<td></td>
</tr>
<tr>
<td>Wang et al., 2013 21</td>
<td>6</td>
<td>298.15–363.15</td>
<td>317.85°</td>
<td>333.05</td>
<td></td>
</tr>
<tr>
<td>Raju and Atkinson, 1990 53</td>
<td>9</td>
<td>273.15–473.15</td>
<td>315.95</td>
<td>374.55</td>
<td></td>
</tr>
</tbody>
</table>

“ΔH° 298 and ΔS° 298 are calculated from temperature dependence of the given ΔG° equation.

Wang et al. and this work, whereas the solubilities of anhydrite from 273.15 to 373.15 K are much larger. Furthermore, neither Wang et al. 21 nor Raju and Atkinson 53 assessed the solubilities of hemihydrate.

The thermodynamic properties of solubility reactions calculated from parameter values in Table 5 are collected in Table 7. As can be seen from the table, enthalpy and entropy changes calculated for the solubility reaction of gypsum by Wang et al. 21 do not agree well with the literature data whereas our model is in good agreement with literature values. For anhydrite, our values are closer to literature values, too. For gypsum and anhydrite, the enthalpy and entropy changes calculated by model of Raju and Atkinson 53 are closer to NBS and CODATA literature values, which is not surprising since their values are based on literature values.

The comparison of Pitzer modeling between this work and previous studies is summarized in Table 8. Our model uses the least Pitzer parameters and gives an excellent agreement for gypsum of 273.15–393.15 K, anhydrite of 273.15–573.15 K, and also hemihydrate of 273.15–473.15 K. All these verify that the assessment of this work is simple and accurate.

4.5. Comparison with Independent Data. The quality of our model is tested by comparing calculated activity coefficient data with experimental data at 298.15 K as well as activity of water on the ice curve. Neither of these data sets or similar data was used in the assessment; only solubility data was used.

The calculated activity coefficient compared with values obtained by Lilley and Briggs 73 is shown in Figure 6 with the estimated experimental error. Lilley and Briggs 73 used a value of −352.6 mV for standard electrode potential of the (Hg)Pb/PbSO4 electrode when obtaining values for the activity coefficient. We also recalculated their results using the recent value of −352.0 ± 0.5 mV for this electrode determined by
The difference by measured and calculated activity coefficients is shown in Figure 7.

Figure 7. Deviation plot of the calculated and experimentally obtained activity coefficient $\Delta \gamma = \gamma_{\exp} - \gamma_{\text{calc}}$ obtained by two different values for standard potential for lead amalgam-lead sulfate electrode (see the text).

The MAPE (AARD%) values for original and recalculated data for the activity coefficient are 2.15 and 2.06%, respectively. Both Pitzer and Mayorga and Rogers used activity or osmotic coefficient data from the literature in their assessment of Pitzer parameters for CaSO$_4$ at 298.15 K. Their Pitzer parameters yield MAPE (AARD%) values for Lilley and Briggs original data to 1.53 and 1.65% and for recalculated data to 1.53 and 0.93%, respectively. All of these results favor a value $-352.0 \text{ mV}$ for the standard electrode potential of the (Hg)Pb|PbSO$_4$ electrode.

Brown and Prue measured the freezing point depression of CaSO$_4$ with a precision of $\pm 0.0002 \text{ K}$. The measured freezing point depression and the calculated osmotic coefficient on the ice curve are put together in Table 9.

As can be seen from the table, our model predicts both measured osmotic coefficients and thermodynamically estimated osmotic coefficients with a standard deviation (SD) of 0.004 and a maximum error of 1.43%.

In a dilute solution, the accuracy of concentration measurements is greater. The difference of modeled water activity on the ice curve from experimental and theoretical activity of water is displayed in Figure 8. As can be seen, our model predicts the activity of water on the ice curve as better than $3 \times 10^{-6}$.

Figure 8. Comparison of calculated to experimental and thermodynamically estimated activities of water on the ice curve.

5. SUMMARY AND CONCLUSIONS

The aim of this study is to give an accurate thermodynamic description of the CaSO$_4$–H$_2$O system and clarify its detailed thermodynamic properties for solution chemistry. The Pitzer activity coefficient approach was used to model the CaSO$_4$–H$_2$O system, and its parameters were assessed from critically evaluated solubility data with MTDATA software. Nine different parameter sets with varying temperature dependencies were tested. It was found that Pitzer parameter $\beta(0)$ is unnecessary for modeling and its value was set to zero, even though it has been adopted in Pitzer modeling by most researchers. Thus, only Pitzer parameters $\beta(1)$ and $\beta(2)$ with simple temperature dependency are required to describe the CaSO$_4$–H$_2$O system from 273.15 to 473.15 K with good extrapolating capabilities.

Table 9. Osmotic Coefficient on the Ice Curve as a Function of CaSO$_4$ Molality

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$m$ (mol/kg)</th>
<th>Brown and Prue$^{75}$</th>
<th>Sippola and Taskinen$^{76}$</th>
<th>this work</th>
<th>$\phi - \phi_{BP}$</th>
<th>$\phi - \phi_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.1376</td>
<td>0.00418</td>
<td>0.7974</td>
<td>0.7980</td>
<td>0.978</td>
<td>0.0004</td>
<td>-0.0002</td>
</tr>
<tr>
<td>273.1359</td>
<td>0.00487</td>
<td>0.7781</td>
<td>0.7788</td>
<td>0.7858</td>
<td>0.0077</td>
<td>0.0070</td>
</tr>
<tr>
<td>273.1348</td>
<td>0.00526</td>
<td>0.7762</td>
<td>0.7773</td>
<td>0.7796</td>
<td>0.0034</td>
<td>0.0023</td>
</tr>
<tr>
<td>273.134</td>
<td>0.00560</td>
<td>0.7672</td>
<td>0.7685</td>
<td>0.7745</td>
<td>0.0073</td>
<td>0.0061</td>
</tr>
<tr>
<td>273.1324</td>
<td>0.00625</td>
<td>0.7548</td>
<td>0.7574</td>
<td>0.7656</td>
<td>0.0108</td>
<td>0.0082</td>
</tr>
<tr>
<td>273.131</td>
<td>0.00670</td>
<td>0.7612</td>
<td>0.7627</td>
<td>0.7599</td>
<td>-0.0013</td>
<td>-0.0028</td>
</tr>
<tr>
<td>273.13</td>
<td>0.00714</td>
<td>0.7549</td>
<td>0.7534</td>
<td>0.7547</td>
<td>-0.0002</td>
<td>0.0013</td>
</tr>
<tr>
<td>273.1294</td>
<td>0.00742</td>
<td>0.7460</td>
<td>0.7467</td>
<td>0.7515</td>
<td>0.0055</td>
<td>0.0048</td>
</tr>
<tr>
<td>273.1282</td>
<td>0.00782</td>
<td>0.7498</td>
<td>0.7497</td>
<td>0.7472</td>
<td>-0.0026</td>
<td>-0.0026</td>
</tr>
<tr>
<td>273.1251</td>
<td>0.00915</td>
<td>0.7318</td>
<td>0.7319</td>
<td>0.7341</td>
<td>0.0023</td>
<td>0.0022</td>
</tr>
<tr>
<td>273.1244</td>
<td>0.00937</td>
<td>0.7352</td>
<td>0.7348</td>
<td>0.7321</td>
<td>-0.0031</td>
<td>-0.0027</td>
</tr>
<tr>
<td>273.1243</td>
<td>0.00952</td>
<td>0.7266</td>
<td>0.7260</td>
<td>0.7308</td>
<td>0.0042</td>
<td>0.0048</td>
</tr>
<tr>
<td>273.1218</td>
<td>0.01046</td>
<td>0.7240</td>
<td>0.7250</td>
<td>0.7229</td>
<td>-0.0011</td>
<td>-0.0021</td>
</tr>
<tr>
<td>273.1207</td>
<td>0.01092</td>
<td>0.7206</td>
<td>0.7216</td>
<td>0.7193</td>
<td>-0.0013</td>
<td>-0.0023</td>
</tr>
<tr>
<td>273.1206</td>
<td>0.01100</td>
<td>0.7197</td>
<td>0.7188</td>
<td>0.7186</td>
<td>-0.0011</td>
<td>-0.0001</td>
</tr>
</tbody>
</table>

SD 0.0041 0.0037
The model of this work is in good agreement with experimental data up to 393.15, 473.15, and 548.15 K for gypsum (CaSO$_4$·2H$_2$O), hemihydrate (CaSO$_4$·0.5H$_2$O), and anhydride (CaSO$_4$), respectively. The absolute average relative deviations between calculated values and adopted experimental data were 2.2, 2.5, and 7.3% for gypsum, anhydride, and hemihydrate, respectively. The transformation temperatures of CaSO$_4$·2H$_2$O to CaSO$_4$(s) and CaSO$_4$·0.5H$_2$O are determined as 315.95 and 374.55 K, respectively, agreeing with most previous researches. The stable temperature range is 273.15–315.95 K for gypsum and above 315.95 K for anhydrite, whereas hemihydrate is a metastable phase in the whole temperature range.

The model of this work was also compared with other previous Pitzer models. The model of Wang et al.\textsuperscript{21} agrees well with solubility data but fails to predict correctly the thermodynamic properties of the gypsum solubility reaction. The CaSO$_4$·H$_2$O model by Rauj and Atkinson\textsuperscript{53} is based on thermodynamic values of solubility reactions and Pitzer parameters obtained from the literature. Even their model describes the NaCl–CaSO$_4$·H$_2$O system adequately; it fails to predict the solubility in binary system CaSO$_4$·H$_2$O, especially in metastable regions. Both these models use more than four terms in their Pitzer parameters.

The model was verified using independent activity coefficient and osmotic coefficient data not used in the assessment, which was based only on solubility data. Our model predicts the activity coefficient at 298.15 K with mean absolute percentage error (MAPE) 2.15% and activity of water on the ice curve better than $3 \times 10^{-6}$. These results suggest that using the Gibbs energy difference as a dependent variable, the new optimizing strategy was successful.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.9b00112. Calculated solubility of CaSO$_4$ from 273.15 K up to 473.15 K (XLSX)

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Notes
The authors declare no competing financial interest.

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REFERENCES


(23) Azimi, G.; Papangelakis, V. G. The solubility of gypsum and anhydrate in simulated laterite pressure acid leach solutions up to 250 °C. Hydrometallurgy 2010, 102, 1–13.


(49) Pihlasalo, J.; Davies, H. J.; Taskinen, P. A. Validation of a New Pitzer Type Model and Database for Aqueous Solutions with Outotec HydroCopper Process Data, Paper Presented in CALPHAD XXXVII, 2008.
